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Problems in Modern Chemistry

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This review deals with the fundamental problems and the main directions of modern chemistry whose current developments offer both immediate and prospective practical advantages while stimulating continuing progress in chemistry and in related areas of science and technology.

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I. INTRODUCTION

In sciences (as in any other creative activity) the creative process is less important than its outcome, and seeking is less important than finding. However, finding without seeking is an exceedingly rare occurrence, and therefore most of the effort, expenditure, and resources in science are devoted to seeking. Modern science is an expensive undertaking, and society cannot allow its scientists to engage in aimless searches. Of course, one can stumble on something interesting and valuable even on the path of aimless research, but no serious research worker will wish his success to be determined by the laws of chance. Every investigation, every scientific endeavour should have a declared aim, and should be able to predict the practical results and potential applications of the work and to evaluate its contribution to related fields of science.

Modern chemistry is a many-sided undertaking, involving extensive enquiries in many different directions. Many of its branches have developed into sciences in their own right (inorganic chemistry, colloid chemistry, radiochemistry, organic chemistry, analytical chemistry, physical chemistry, crystal chemistry, chemical physics, electrochemistry, geochemistry, biochemistry, polymer chemistry, etc.). Each of these sciences has its own objectives and well defined boundaries, its own problems, its experts, and its acknowledged leaders. However, in modern chemistry we find many fundamental problems which are common to a variety of areas of enquiry: these attract the combined attention of all branches of chemistry and stimulate contributions from all chemical sciences, whatever their specific objectives and problems. It is important to recognise these "cosmopolitan" problems so as to formulate clearly the most important directions in which further advances can be expected and to achieve greater coherence, relevance, and therefore also effectiveness of the work.

The aim of this review is to define the most important problems in modern chemistry, to present a predictive analysis of their recent developments, and to identify the most timely and relevant achievements.

II. CHEMICAL STRUCTURE AND FUNCTION

The number of known chemical compounds (approximately eight million at present) is still growing rapidly. The atomic-molecular architecture and electronic structure of these compounds (whether extracted from naturally occurring materials or synthesised) vary between wide limits. Their physical and chemical properties, and therefore also their functions, show similarly extensive variations. In order to identify a substance having prescribed properties and applications (i.e. a prescribed function) we usually need to examine between 3 and 10 thousand compounds: the ambitious task of converting a prepared compound into a substance aimed specifically at serving mankind and at advancing civilisation has a disappointingly low effectiveness. Clearly, establishing a relation between the electronic structure of a compound or material and its functional behaviour is a problem of fundamental importance, which must be solved if we wish to predict the function and usefulness of a substance. In practice the inverse problem is even more important: how should a substance be constructed, what should be its molecular architecture and electronic structure, in order to achieve a prescribed set of properties and a required function?

Modern chemistry has had some undeniable (though modest) successes, based on a rich and varied stock of experimental results, in the solution of both the direct and the inverse problem. We can now confidently predict the dependence of the polymerisation behaviour of monomers on their structure, the main types of chemical reaction and the reactivity of various functional groups, the changes in the electrophysical properties of semiconductors caused by changes in their structure, etc.

A clear example of a successful search for the relationship between structure and function is provided by the synthesis of organic and metal-organic electrical conductors: molecular metals (see Chapter V). Thus the compound $Hg_{3-\delta}AsF_6$, synthesised in 1971, has a high, typically metallic conductivity, and becomes a superconductor at low temperatures. Chemical analysis gives this compound the composition Hg_3AsF_6, but

the geometric dissimilarity between the position of the constituent atoms in the crystal lattice produces vacancies of AsF_6 groups, so that the composition of the unit cell becomes $Hg_{3-\delta}AsF_6$, where $\delta = 0.18$. The unit cell of a crystal of this compound (Fig.1) shows an unusual molecular structure, consisting of two components: a framework of AsF_6^- anionic octahedra and cationic chains of mercury atoms, accommodated within the channels of the anionic framework along the principal axes (*a* and *b*) of the crystal.

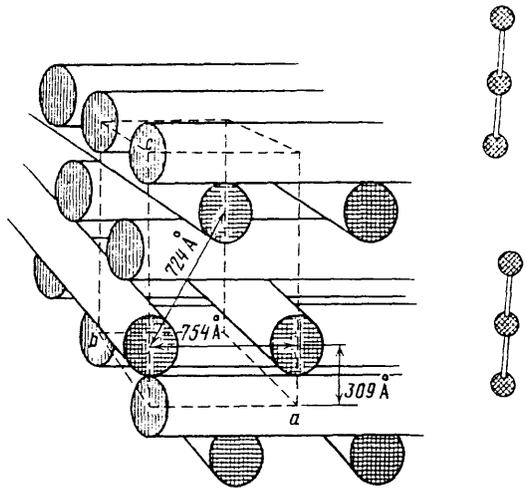


Figure 1. Molecular-structural organisation of $Hg_{3-\delta}AsF_6$; the cationic chains of atoms are shown as cylinders, between which are located the anionic AsF_6 octahedra.

This structure imparts special electrical conduction features to the material. The chains of mercury atoms behave as a one-dimensional ordered metal with a high conductivity. This feature results in an electrical conductivity in the crystal along the chains (i.e. in the *a* and *b* directions), coupled with a low conductivity in the perpendicular direction (i.e. along the *c* axis). Lowering the temperature activates the interaction between the conducting chains (first the parallel, and then the perpendicular), leading to superconductivity at temperatures below 4.1 K.

The most important feature of this crystal structure are the linear chains of atoms with delocalised (generalised) electrons, which are responsible for the new function of the material: its metallic conduction and superconductivity. The concept of this structural feature is exploited in all attempts to synthesise molecular metals: organic substances in which π-electron molecules are packed in the crystal as one-dimensional chains with overlapping delocalised π electrons. The motion of the electrons along the chains is responsible for electrical conduction in these compounds, and occasionally for superconductivity at low temperatures (see Chapter V). The structure of one typical organic superconductor, [*bis*(ethylenedithiolo) tetrathiofulvalene]$_2^+I_3^-$, is shown in Fig.2.

Establishing the correlations in the structure–property–function chain is the scientific aim of chemical materials science, and is directly relevant to the development of any new material (polymers, phosphors, materials for semiconductor and laser technology, chemical reagents and catalysts etc.) It is especially important in biochemistry and medicine, where the functional properties of medicinal preparations, hormones, and other physiologically active compounds determine their functional effects in living organisms. This is a very large field, which includes major topics such as the chemistry of memory and the chemistry of thought (a relatively obscure subject, with fundamental practical and intellectual connotations).

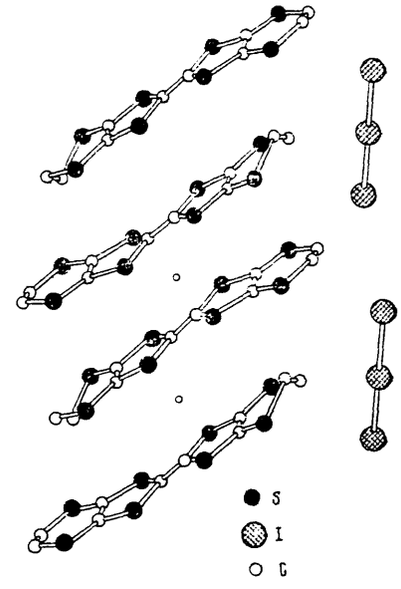


Figure 2. Projection of the crystal structure of the organic superconductor [*bis*(ethylenedithiolo)tetrathiofulvalene]$_2^+I_3^-$.

We can solve the direct problem, i.e. establish the structure–function relationship, at two distinct levels: the empirical level, confined to a simple formulation of the relationship between structure and function, and the non-empirical level, involving the study and the identification of the atomic-molecular mechanism by which a given structure can fulfil its function. However, modern chemistry can often formulate and solve the inverse problem: to create a structure having a prescribed function. For example, substances having oxidising properties stronger than those of normal oxidisers (F_2, PtF_6, RhF_6, IF_5, etc.) are needed in chemical synthesis. Compounds of the "inert" elements (xenon and krypton) were obtained by using the new oxidisers. The strongest oxidisers (ICl_5, AuF_6) should activate other elements of Group VIII, and induce previously unreported chemical reactions. This hope is not unrealistic: not many years ago the preparation of chemical compounds of xenon would have seemed out of the question, and yet these compounds are now a conventional part of the chemist's working arsenal. Stable organic paramagnetic materials are now equally familiar: the nitroxyl radicals, which offer a range of functions and are therefore

widely used in physics, chemistry, molecular biology, medicine, and technology.

A similar problem can be formulated in respect of high-energy substances, involving the search for chemical structures with a high energy content. One path to this goal is the synthesis of compounds with atoms in unusual valency states or with an unusual hybridisation of chemical bonds (for example, organic compounds containing a non-tetrahedral saturated carbon atom). This type of problem can (and should) be formulated in all branches of chemistry.

Quantum theory has a large part to play in solving these problems, and its status and role in modern chemistry are beginning to change very markedly. Whereas the task of quantum chemistry was previously to seek (often, successfully) an explanation of the physical origin of various chemical phenomena and structural-chemical effects, its principal aim is now the theoretical prediction of chemical structures, of their existence regions and stability conditions, and of whether their synthesis can be realistically attempted. In this sense quantum chemistry has now moved into the front rank of chemical science, where it directs the experimenters towards molecules and substances with realistic thermodynamic and energy parameters. This new style of quantum chemistry is already apparent from the effort now devoted by quantum chemists to calculations of "exotic" molecules (for example, molecules with a non-tetrahedral carbon atom, hypermetallic molecules, hypothetical "spherical" molecules containing 120 or 60 carbon atoms in sp^2 hybridisation, with a high electron density inside the sphere. The molecule with 60 atoms has been called footballene because of its outward similarity to the ball used in that game).

Both the chemical structures and the functions of substances are extremely varied, and the relationships between them are even more varied; the development of adequate systematics is therefore an urgent problem at present. Existing classifications distinguish types of substances by structure-chemical criteria (aldehydes, sulphides, ketones, fluorides, olefins, chalcogenides, etc.) rather than by functions. Modern chemistry requires, in addition, a systematisation based on the structure–property–function principle. Computer-accessible chemical data-bases should play an important part in its development (banks of structural-chemical and functional data, computer systems for identifying and distinguishing chemical compounds according to their functions, etc.). The development of these new methods of classification and the establishment of relationships in structure–property–function series should offer an effective and clear strategy of scientific enquiry in the field of chemistry.

III. CONTROL OF CHEMICAL PROCESSES

The complexity of chemical processes can be both troublesome and advantageous to the chemist: it allows the adoption of a flexible hierarchy of methods of process control at various levels, from the atomic–molecular level to the level of supermolecular organisation and organisation in terms of mass and energy transfer, aimed at establishing a state of concentration and energy "comfort" for the chemical process.

A chemical reaction is a physical process resulting in the regrouping of atoms and the rearrangement of electronic shells, leading to the conversion of the initial species (reagents) into the final products. The process is controlled by two fundamental characteristics: energy and angular momentum (the moment of the quantity of motion). The importance of the former has long been recognised in chemical science, whereas the role of angular momentum in chemical reactions was recognised only recently.

The great majority of chemical reactions require additional energy to be supplied to the reacting species in order to overcome an energy barrier. The height of this barrier (or, in other words, the amount of energy to be supplied to a particle to allow it to react) is a problem for which a general solution has not yet been found. Theoretical calculations of barriers and of potential energy surfaces for chemical reactions by the most recent techniques of quantum chemistry (non-empirical or semi-empirical) have failed to solve the problem so far: they are cumbersome, their scope is limited, and they are often unreliable. Many empirical relationships for calculating energy barriers and reaction rates (Polanyi's rule, Hammett's equation, Tafel's law, the Woodward–Hoffman rules, the Brønsted–Winstein relation, etc.) are also of limited application as well as being only rough approximations. On the whole, the problem of chemical reactivity—i.e. of the relationship between the electronic and nuclear structure of chemical species and the rate (or barrier height) of their reactions is a classical on-going problem, still far from being solved. This is mainly because the range of chemical species (atoms, molecules, ions, radicals) is enormous, offering a wide range of Coulombic or exchange interaction potentials and of chemical reaction paths. The multitude of types of electron shell and of paths available for their transformation prevents the development of a single, general quantitative theory of chemical reactivity, though in terms of theoretical physics the most elementary chemical interactions are relatively simple and consist exclusively of electromagnetic interactions (nucleus–nucleus, electron–electron, and electron–nucleus).

Controlling a chemical reaction, i.e. changing its rate or its direction, implies firstly changing the height of the energy barrier and secondly adding energy to the internal degrees of freedom in a form usable by the chemical species in overcoming the barrier.

The first control principle is chemical: it relies on modifying the electron shells of the reacting particles by solvation or complex formation. The study of solvation with the aim of discovering effective means of controlling the reactivity and the direction of chemical reactions is one of the main topics of modern chemistry. The main contribution to solvation effects usually comes from complex formation. Modern physical methods have led to important advances in our understanding of complex formation: direct evidence of the delocalisation of the electron shells of the partners in the complex has been obtained, the electronic orbitals involved in the "joint" between the partners have been identified (in some cases), the main types of complex have been recognised and the diagnostics and criteria of complex formation have been formulated, the structural, physical, and dynamic properties of many complexes have been determined, and it has been established that even in the gas phase, chemical reaction is often preceded by complex formation.

Complex formation should affect the reactivity of any chemical species, since it influences the distribution of electric charges, the energy of the molecular orbitals, and the geometric screening (and therefore also the energy barrier) which the reaction must overcome. A much more difficult problem is to establish the extent and the direction of the resulting change in chemical reactivity: is the chemical activity of the reacting particles enhanced or suppressed by the complex formation? The question is not easily answered, and the answer cannot be general or unique. It depends on two factors of fundamental importance: 1) is the complex located on the correct reaction coordinate, and 2) how often do the reacting particles pass over the energy barrier in the direction of the reaction coordinate, and is the transition adiabatic or non-adiabatic. Many examples of activation and of passivation of chemical species by complex formation have been

reported; in some cases partial rules (applicable only to some types of reaction) have been established, but there are as yet no general principles allowing the reliable prediction of complex formation and reactivity effects.

These comments are equally applicable to solvation effects. The solvation concept is a more general one, and includes electrostatic effects as well as complex formation effects. The contribution from electrostatic interactions to chemical reactivity is not yet fully understood. There is evidence that the contribution has often been overstated, since chemical reactions between particles (even charged) are mainly short-range effects, involving exchange interactions rather than long-range Coulombic forces.

Being chemical methods of controlling the chemical reactivity of particles, complex formation and solvation often affect the mechanism of chemical reactions by varying the composition of the reacting species (free ions or ion pairs, radicals and their complexes, molecules and molecular associations, isolated atoms and clusters, etc.). The term reaction mechanism denotes the succession of elementary chemical processes which convert the initial substances into the final products. The mechanism is usually identified from the composition of the final and of the intermediate products, from the kinetics of disappearance of the reacting particles and of the formation of intermediates and products, from the composition of the intermediate active species (detected by physical methods), etc. We now have fairly reliable methods, indications, and criteria for establishing reaction mechanisms, but in general the formulation of a reaction mechanism in full detail remains a difficult problem which is only rarely (and not always unambiguously) solved.

Finding the mechanism is not an end in itself: it is a necessary stage in the determination of the rate-limiting step and in identifying the principal and the secondary reaction paths. The final aim is to find an effective method of controlling the chemical process and of increasing its yield and selectivity. Thus the identification of the mechanism is an important step forward towards the creation of highly selective, fast, and low-energy chemical technologies.

The discussion so far has been limited to chemical methods of controlling reactions; physical methods of stimulating and controlling chemical reactions involve the transfer of energy into the internal degrees of freedom of the reactants in an amount sufficient to overcome the energy barrier. Exposure to light, radiolysis, and plasmas are all physical methods of stimulating reactions by injecting energy into the electron shell. In most cases the electronically excited species thus formed have a high reactivity and react almost with a zero activation energy. However, this method of stimulating reactions has the following disadvantages: firstly, electronically excited states can react differently from the ground state, and therefore physical stimulation is often accompanied by a change of mechanism and a change in the composition of the final products; secondly, in the vast majority of cases the energy transfer process has a low efficiency, and only a small fraction of the energy supplied to the system is used in the chemical transformation.

Infrared lasers can pump energy into vibrational degrees of freedom, and they are often used to stimulate chemical reactions. This work has attracted a great deal of interest in recent years, and it has been shown that vibrational excitation is effective in overcoming the endothermic part of an energy barrier while having almost no effect on barrier crossing in thermally neutral or exothermic reactions. Thus the laser dissociation of molecules and the associated methods of isotope separation are now well established. These are endothermic processes, involving the energy pumping of vibrational levels. In neutral or exothermic reactions the utilisation coefficient of the vibrational energy to give chemical reaction is not more than 1–2%.

Mechanical activation can be an important source of stimulation in chemical reactions (for example, process in shock waves, at high pressures, under conditions of shear deformation, etc., see section VI). We know that mechanical deformation produces unusual chemical reactions, accompanied by luminescence, electron emission, and electric discharges. Similar effects are observed in phase transitions and structural rearrangements in crystalline solids. An unusual phenomenon was discovered recently: low-temperature "explosions", in which the elastic energy stored in glasses at low temperatures induces fast chemical reactions at temperatures below the boiling point of liquid helium. The paths and the physical principles by which the mechanical energy is converted into chemical energy are not yet understood, and their identification is an important problem whose solution may stimulate the development of new technologies and of a new type of chemical energetics (section VII).

As well as being energy-forbidden, chemical reactions can be forbidden in respect of the angular momenta of the reacting particles. This quantity must be conserved, and reactions involving a change in angular momentum are forbidden: only reactions not accompanied by a change in angular momentum are allowed.

Many chemical reactions require a change in orbital angular momentum; however, the orbital momentum rule is not rigid, since this momentum is strongly coupled to the motion of the molecule as a whole, and is transferred to external degrees of freedom. The rule with respect to spin angular momentum is much more strict: this appears in reactions involving free radicals, in the reactions of triplet molecules and ions, and in many other reactions involving paramagnetic species. The recently discovered magnetic effects in chemical reactions are the physical result of the spin angular momentum rule. They include spin polarisation of electrons and nuclei, the effect of external magnetic fields on the reaction, the magnetic isotope effect, and radio-frequency emission in chemical reactions. These newly discovered properties of chemical reactions involving radicals open new approaches to the control of reactions by using d.c. magnetic fields, or radio-frequency and ultra-high frequency electromagnetic fields, to influence electronic and nuclear spins and to remove the spin angular momentum rule. This new branch of chemistry (we could call it "spin" chemistry) is developing rapidly, and recent progress in this area has resulted in new methods of studying chemical reaction mechanisms and in the formulation of chemical radiophysics and of new principles for separating nuclear isotopes and isomers.

IV. MOLECULAR AND SUPERMOLECULAR ORGANISATION OF CHEMICAL PROCESSES (MOLECULAR DESIGN)

The vast majority of chemical reactions used in industry and in science belong to the "non-organised" type, i.e. the participating species react through collisions which are random in time, in location, and in the mutual orientation of the particles. In other words, there is no molecular or supermolecular organisation of the chemical interaction in space and time.

On the other hand in molecular biology an entirely different situation exists: molecular and supermolecular organisation is a characteristic property of biochemical processes (for example, the synthesis of proteins, the transport of ions and other substances through membranes, electron transport along a chain of cytochromes and the associated phosphorylation, photosynthesis, enzyme catalysis, etc.). Enzymes can bind and orient the reagents, and thus organise the elementary

chemical acts and produce a high level of stereospecificity, reagent selectivity, and selectivity of reaction type, of localisation of the reaction, of temperature and pH, etc. In biochemical processes not only the elementary acts but also whole cascades of reactions are organised: for example, in photoreception processes each light quantum absorbed by the retina in the eye triggers a large cascade of chemical reactions which produce (in quantum yields up to 10^4) cyclic guanosine monophosphate, producing an electric potential in the membrane which later appears in the brain as the result of the light perception. Because of their high level of organisation biochemical reactions achieve a selectivity, functionality, and operating speed which cannot be matched by ordinary chemical reactions.

Examples of supermolecular organisation of processes in cheimstry are still few. An unusual example is the interaction of methyl radicals with palmitic acid (C_{16}). In ordinary, "non-organised" chemical processes the most reactive site in the molecule is the α position, adjacent to the carboxylic acid group. On the other hand if the molecules of the acid are organised as a two-dimensional layer on a water surface the attachment of methyl radicals (formed by an electrical discharge or by irradiation of methane in the gas phase) takes place at the "tail" of the molecule and is accompanied by an increase in the length of the molecular chain (forming the C_{17}, C_{18}, etc. acids). This is a striking example of the molecular organisation of an ensemble on the reactivity (and even the direction) of a chemical reaction. This reaction is believed to have played an important role in the chemical evolution of life on Earth, since it can account for the synthesis of the initial substances used in the construction of biological membranes.

The simplest method of supermolecular organisation in chemical reactions relies on the use of molecular beams to deposit the reacting layers according to a given programme (layer thickness, periodicity, etc.) in order to prepare chemical compounds and compositions. In particular, this principle can be used to produce semiconductor structures and solid-state superstructures—crystals grown by depositing semiconductor layers a few atoms thick with a strictly periodic alternation of *n*- and *p*-type doping. These new materials offer a unique set of electrophysical properties and now have an important place in semiconductor technology and solid-state physics. Their preparation by the ordinary methods of "non-organised" chemistry would be impossible.

The structural elements which determine the molecular and supermolecular organisation of chemical processes could be micelles, vesicles, adsorbed monolayers, molecular membranes, clathrates, liquid crystals, clusters, interfacial boundaries, etc. There are known examples of the use of these structures in chemistry (interfacial catalysis, catalyst immobilisation, etc.). In these systems space–time organisation and periodic oscillations in properties are possible. For example, in the water–oil system in the presence of surface-active substances we observe oscillations in pH and in the electrochemical potential similar to those which occur in nerve cells, muscular tissues, and in mitochondria. Other examples of space–time organisation in chemical processes is the periodic precipitation of a solid product during the mixing of two substances (Liesegang rings), the Belousov–Zhabotinskii periodic reaction and its many analogues, the self-oscillations in the rate of many heterogeneous catalytic reactions, etc.

Many important processes cannot be carried out in the framework of conventional ("non-organised") chemistry. Thus, the photosensitised dissociation of water into hydrogen and oxygen (abiogenic photosynthesis, see section VII) requires three elementary stages: photo-generated charge separation, i.e. the formation of spatially isolated electrons and holes, the interaction of the electron with a water molecule (and reduction of the water to hydrogen), and the interaction of the hole with a water molecule (and oxidation of the water to molecular oxygen). The process must be organised so as to prevent the recombination (annihilation) of the electron and the hole, and therefore the reduction and the oxidation of the water must take place on different catalysts.

An example (perhaps not the best) of the molecular organisation of this process is shown in Fig. 3. The catalysts are deposited on opposite sides of colloidal particles of the semiconductor TiO_2 (metallic platinum and ruthenium oxide). The photo-excitation of a sensitiser S results in its ionisation, and an electron is transferred to the TiO_2 either directly or through the intermediate carrier R. The electron then migrates into the conduction band of the TiO_2, it reaches the Pt, and it reduces a water molecule on the platinum. The hole migrates to the RuO_2 and oxidises the water to oxygen on this catalyst.

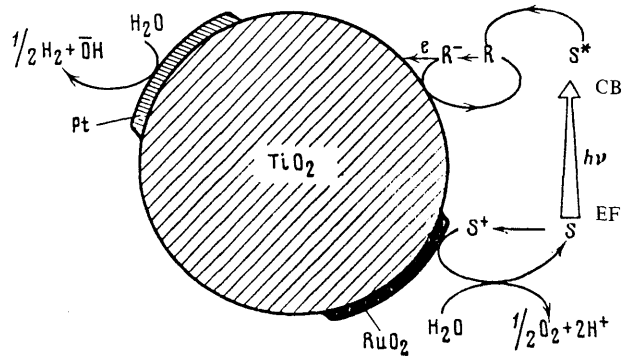


Figure 3. Organisation of abiogenic photosynthesis: EF is the Fermi level, CB is the conduction band.

This very simple version of an organised chemical system actually works, but its efficiency is low because of the many possible side-reactions. Clearly, a more perfect organisation is needed: the basic approach to the solution of the abiogenic photosynthesis problem is to seek a suitable organisation.

The development of organisational principles and the creation of organised chemical systems simulating biochemical systems (biomimetic systems) are among the most general and promising lines of attack used in modern chemistry, and the first tentative steps have already been taken (with some success) in this direction. A good example of a biomimetic system is provided by the calyxarenes (cyclic products of the alkaline condensation of phenols with formaldehyde, Fig. 4). These molecules have a very unusual structure: the benzene rings with their substituents are arranged to form an enclosed space, so that the whole molecule is reminiscent of a vase (and is named from the Greek *calyx*, a vase). This "molecular vase" can have closed walls [in the form of a truncated cone, with a base consisting of the hydroxy groups (Fig. 4c)], or the walls may be partly open if some of the benzene rings are folded outwards, forming windows in the wall of the vase (Fig. 4d).

Because of their special structural organisation the calyxarenes can transfer metal ions through hydrophobic membranes, and they are superior even to crown ethers as carriers. Adding various functional groups to the calyxarene molecules produces catalytic properties simulating those of enzymes.

For example, the calyxarene whose structure is shown in Fig. 4*e* is a model of the enzyme aldolase and has the characteristic functions of this enzyme. We know that similar biomimetic properties are found also in some other molecules (for example, the cyclodextrins, which form inclusion compounds in which the chemical transformations of the substrate take place).

The most obvious supermolecular organisation effects are found in chemical reactions taking place in crystals. In the case of molecules organised as a crystal the intrinsic reactivity

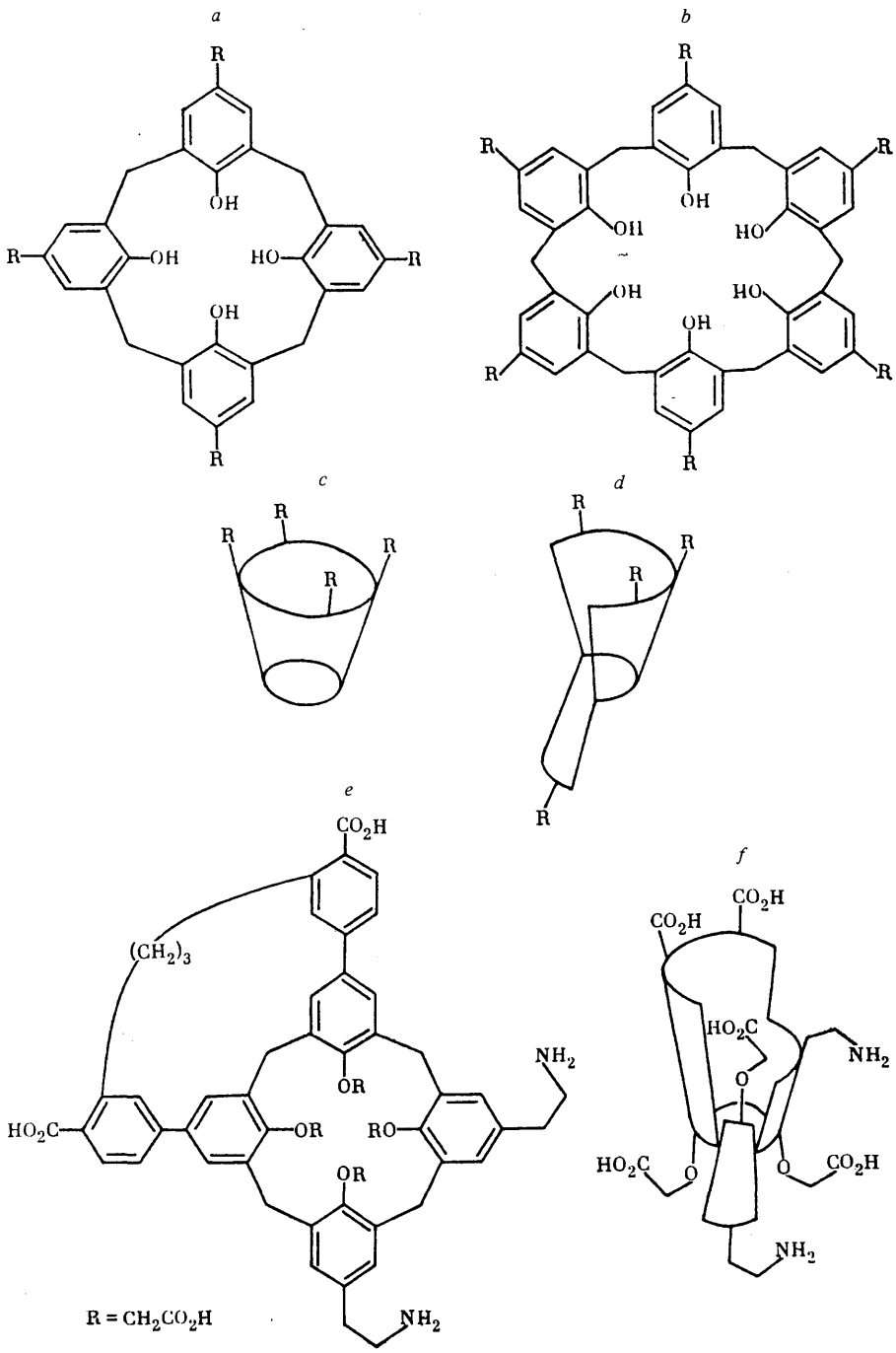
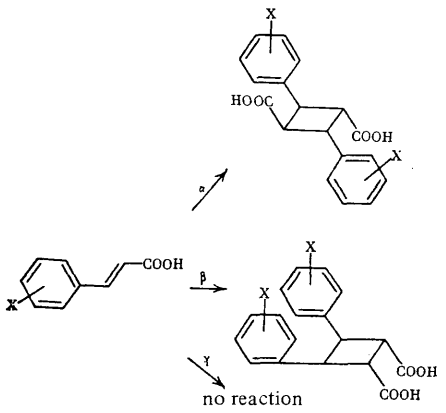


Figure 4. Structural formulae of some calyxarenes and diagrams of their three-dimensional organisation: calyxarene with four (*a*) and six (*b*) benzene rings; the wall of the cavity in calyxarene *a* can be closed (*c*) or partly opened (*d*) through the rotation of one of the four benzene rings; simulation of the function of the enzyme aldolase (*e*) and diagrams of its three-dimensional organisation (*f*).

(determined by the structure of the electron shells) is less important to the course of the reaction than the method by which the molecules are packed and stacked in the crystal. The direction of the reaction is determined by the intermolecular distances in the crystal, by the mutual orientation of the molecules, and by the three-dimensional symmetry of this crystal.

The features of solid-state reactions are clearly seen in the photodimerisation of *o*-ethoxy-*trans*-cinnamic acid:



The α form of the acid crystallises from acetone; it has a centre of symmetry, and neighbouring molecules are packed in a head-to-tail configuration. The product of the photodimerisation is a centrosymmetric molecules which retains the elements of symmetry of the initial pair of monomer molecules. The β form crystallises from benzene; the crystal has a plane of symmetry and the molecules are packed in a head-to-head configuration. The photo-dimerisation product retains the symmetry elements of the initial pair. The distances between double bonds are 3.6–4.1 Å in the α form and 3.9–4.1 Å in the β form. The stacking of the molecules is shown in Fig. 5 for one of the crystal projections; here R denotes the C_2H_5OPh group, and the black rectangle the CO_2H group. The γ form crystallises from aqueous ethanol solution; in this form the stacking of the molecule is unfavourable to the reaction (see Fig. 5), the distance between double bonds is 4.2–5.1 Å, and no reaction takes place.

The polymerisation of substituted diacetylenes (Fig. 6) to give conjugated polymers (organic semiconductors and organic metals, see section V) is determined by the same topological relationships between the structure of the crystals of the monomeric molecule and that of the crystals of the product. The monomeric molecules are organised in the crystal in such a way that only a slight rearrangement of the crystal structure is needed for the polymerisation. The dimer $(NS)_2$ is polymerised in the crystal in a similar way, giving the superconducting polymer $(SN)_x$ (see section V).

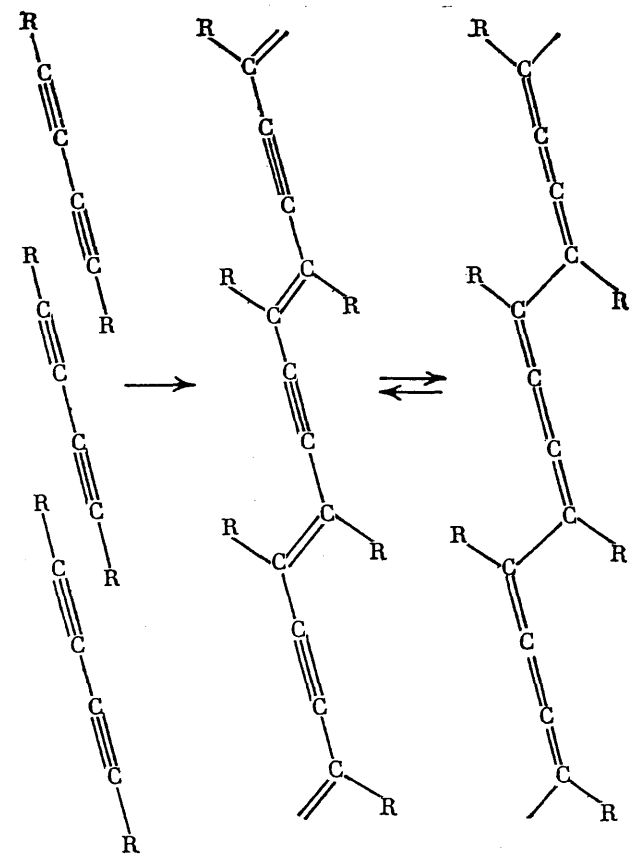


Figure 6. Arrangement of the molecules of diacetylene in the crystal and conversion into a conjugated macromolecule.

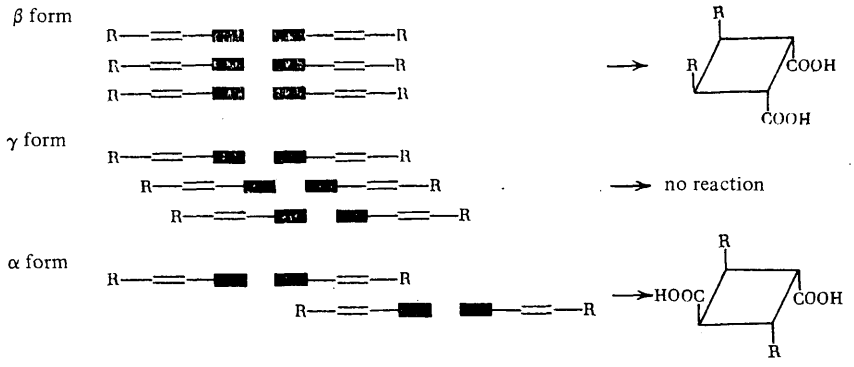


Figure 5. Arrangement of the molecules of *o*-ethoxycinnamic acid in the crystal and corresponding types of chemical reaction.

Pure optically active polymeric structures can also be obtained by the same method through the polymerisation of enantiomeric monomers in their crystalline form.

Crystal structure also allows topochemical control of the photo-induced transfer of a hydrogen atom to the keto group and to the C=C double bond. In the first case only the transfer of hydrogen atoms at a distance of 2.26–2.58 Å from the oxygen atom is allowed, i.e. at a distance smaller than the sum of the van der Waals radii of the H and O atoms (2.72 Å). In the second case atoms at a distance of 2.6–2.89 Å from the carbon atom of the double bond are transferred (again, at a distance smaller than the sum of the van der Waals radii of the H and C atoms, 2.90 Å).

Photo-dimerisation, oxidation ozonolysis, halogenation, and dehydrochlorination reactions also take place with a high stereoselectivity in crystals and on their surfaces. Many examples of extreme selectivity and topological control have been observed for reactions in crystals but not for the same reactions in solutions or in melts.

The organisation of molecules in crystals offers new possibilities of controlling the reactivity of a system and new pathways in synthetic chemistry. Many crystals display a high degree of polymorphism. Thus, methanol can crystallise in two forms (α and β) differing in the symmetry of their unit cell: cinnamic acid (discussed above) has three forms; more than 30 crystal forms are known for crystalline sulphur; many organic substances have several (up to 10 or 12) crystal-chemical modifications. We are eftectively discussing a new branch of chemistry: crystal-chemical engineering, whose objective is the construction of crystals matched to specified chemical programmes.

The molecular and supermolecular organisation of ensembles of reacting molecules (or, in other words, the supermolecular design of chemical reaction) is an important new principle for the control of chemical processes and a valuable asset of chemical engineering. So far this principle has not been fully explored, and few applications have been reported, but we can expect "organised" chemistry to play a leading role in chemical science and technology in the near future.

V. CHEMICAL MATERIALS SCIENCE

Chemistry is the main source of materials for all areas of science and technology, from electronics and metallurgy to agriculture and medicine: in this sense chemistry genuinely stands at the centre of science. The development and evaluation of new substances, preparations, and materials, and the improvement of known or currently used materials, are the principal aims of modern chemistry. Its constituent elements are the synthesis of new substances and materials, the study of their properties, and the analysis of their behaviour under the conditions and regimes to which the materials will be exposed in practical applications. These topics can be combined under the general title of chemical materials science.

A traditional and ever-present problem is the development of highly stable inorganic materials: glasses and vitreous-crystalline materials (glass ceramics and ceramics). Important advances have been made in these topics, including the production of high-quality optical, heat resistant, and semi-conducting glasses with a high mechanical strength, thin-film and lamellar glasses with a high elasticity and thermal and dielectric strength, etc. Porous glasses with pores and channels of a given size (down to 10 Å or less) have been developed for use as filtering media (in particular, in the filtration of biomolecules, viruses, etc., and in the preparation of pure microbiological cultures).

New types of ceramic with a high mechanical, chemical, and dielectric strength have been obtained. These have a low thermal expansion coefficient, and they are widely used in technology, electronics, and radio. Metallic glasses have also been prepared: amorphous, vitreous metals with a high chemical stability and corrosion resistance.

Inorganic composite materials consisting of fibres in a metallic or ceramic matrix offer very attractive prospects. They can satisfy two apparently incompatible requirements: high strength and high crack resistance. For example, the boron-aluminium composite developed at the Solid-state Physics Institute of the USSR Academy of Sciences has a strength of 100–150 kgf mm^{-2} (in the armouring direction), an elastic modulus of ~25000 kgf mm^{-2}, and a density of 2.7 g cm^{-3}, i.e. it combines the mechanical properties of a good quality steel with the density of aluminium. Ceramic fibre composites have a work of fracture an order of magnitude greater than that of the best homogeneous ceramic, and they can be used to produce light-weight components able to withstand hostile mechanical and thermal conditions.

Problems currently studied still include the development of corrosion-resistant alloys and materials, of inorganic semiconductors, photoresists, light detectors and photoelectric energy converters with a high quantum yield and a high selectivity and sensitivity towards chosen regions of the optical spectrum, and the development of piezoelectric, ferroelectric, and other materials for acousto-electronics.

Improvements are being sought in mineral fertilisers of high food value, assimilability, and optimum composition, in new rubbers based on polyurethanes and polysiloxanes, fluororubbers, etc., offering a high thermal and chemical resistance, frost resistance, and good elastic and relaxation properties, in new plastics, resins, and ion-exchanger materials and adsorbents, in long-life lubricants and viscosity additives, in lacquers with a high adhesion and high-grade electrical insulation and anticorrosion properties, in glues, sealants, and surface-active substances and coatings, in porous and filtration media for separating and purifying substances in the food industry, in technology, and in medicine, and in strong fibres (both synthetic and modified natural fibres), etc.

The development improved or new pigments, phosphors, scintillators, and laser generation materials is a continuing problem. Light-fast dyes are needed for optical lasers, laser shutters, and modulators. New substances are being developed for chemical light sources (substances which resemble luminol in converting chemical energy into light energy with a high efficiency).

Polymer materials and their most recent modifications (polymer composites) occupy an important place in modern materials science. Current developments include various composites reinforced with organic or inorganic fibres (glass, boron, asbestos, graphite, and carbon fibres, and fibres based on boron nitride, TiO_2, Al_2O_3, etc.). This wide variety of composites offers a wide range of useful properties: electrical strength, chemical stability, elasticity, mechanical strength in shear and compression, resistance to plastic flow, etc. Further substantial improvements in the mechanical and thermal strength of these composites can be expected when the fundamental problem of lowering the concentration of localised stresses at the fibre–polymer matrix interface has been solved. Various approaches to this problem are being studied: for example, by inserting a boundary layer with an elastic modulus intermediate between those of the fibre and of the matrix, or by applying artificial elastic deformations to the boundary to suppress (or compensate) the main stresses generated between the fibre and the matrix. The same problem arises in the development of high-strength inorganic composites.

Dispersion-strengthened or filled (usually with an inorganic filler) polymer materials are similar to polymer composites. With all these materials the material production stage can be by-passed, and the article can be formed directly, but this requires a very precise and reliable control over the properties of the chosen composite.

Other important materials include incombustible or fire-resistant coatings and cloths, and anti-static materials for use in situations where electrification or static electricity can present sanitary, explosion, or fire hazards (floor coverings in computer rooms or in medical X-ray rooms, materials for protective clothing in tanker fleets, in the petrochemical and gas industries, etc.). Light and cheap (preferably organic) materials are also needed for protecting electronic and radio equipment from stray electromagnetic fields, and for absorbing electromagnetic radiation.

Methods of preparing entirely new materials (organic semiconductors and metals) have been discovered in recent years. Their precursors were the polymers with a conjugated π-electron system (polyacetylene, polyphenylene, etc.), prepared by polymerising the appropriate monomer in solution; these were amorphous substances with a high concentration of defects, a low electrical conductivity, and a poor chemical stability towards oxygen and other reagents. An important step forward was made by the production of perfect (almost defect-free) conjugated polymers by polymerising the monomers in crystals (see section IV). Another success was the discovery of ways of modifying the conduction properties of organic semiconductors by treatment with bromine, iodine, AsF_5, or inorganic salts: this operation (doping, or alloying) creates local impurity centres in the semiconductor structure and results in a large increase (by 10–11 orders of magnitude) in the concentration and mobility of the charge carriers and therfore also in the conductivity of the material. This type of doping converts polyacetylene (for example) into a substance with an almost metallic conductivity. Furthermore, thin films of these conjugated polymers prepared by polymerising the monomer in a crystal offer unique and reversibly controllable thermal and optical properties.

Organic batteries and accumulators with potentials up to 4.5 V and capacities up to 300 W kg^{-1} have been produced from doped conjugated polymers. According to estimates made in the USA the scale of production of organic semiconductors (for electronic applications only) was 10000 tonnes in 1981, and had doubled by 1984. They are used in electrical noise suppression systems, in cable sheaths, in accumulators and current sources, in photovoltaic apparatus and converters, and in micro-electronic circuits. Further improvements can be expected, and the new materials with improved electrophysical properties have a promising future.

A good example of a successful development in chemical materials science is the discovery of an entirely new type of substance: organic metals. These are organic compounds with a crystalline molecular organisation which results in a high electronic conductivity (up to $10^5\ \Omega^{-1}\ cm^{-1}$), approaching that of the best metallic conductors (for example, mercury). Typical materials of this type are the ion-radical salts, in which the cation is a radical such as tetrathiafulvalene (TTF), tetraselenafulvalene (TSF), tetramethyltetraselenafulvalene (TMTSF), etc., and the anion is a radical such as tetracyanoquinodimethane (TCNQ) or its dimethyl derivative (DMTCNQ), or an inorganic anion (PF_6^-, AsF_6^-, etc.). In crystals of these compounds the cation radicals are stacked with their planes in a parallel orientation, forming small stacks (one-dimensional chains in which strong interactions between the electrons of the π system develop, producing a high electrical conductivity). The anions are also arranged in one-dimensional chains, parallel to the cation chains (the molecular organisation of these crystals is discussed in detail in section II).

Organic metals have a high electrical conductivity (up to $10^3\ \Omega^{-1}\ cm^{-1}$) even at room temperature; at lower temperatures their conductivity is still higher. For example, it is $10^5\ \Omega^{-1}\ cm^{-1}$ for $(TMTSF)^+(DMTCNQ)^-$ near 40 K, and $10^4\ \Omega^{-1}\ cm^{-1}$ for $(TMTSF)^+(ClO_4)^-$ at 50 K. The one-dimensional packing of the conducting cation chains results in a highly anisotropic conduction: the ratio of the conductivities along and across the chains is 500–1000.

The behaviour of the organic metals includes two surprising features. The first stems from the instability of the one-dimensional chains, predicted by Peierls in 1954, and consists in a change from a uniform distribution to an alternation of intermolecular distances at low temperatures, producing waves of charge density (or spin waves in the case of chains of paramagnetic particles). Because of the alternation of intermolecular distances in the one-dimensional chain the energy band containing the levels of the valency π electrons splits into two systems of levels: a lower system, filled with electrons, and an upper, empty system. In order to cause conduction we must transfer an electron from the filled into the empty system, i.e. we must surmount the energy barrier separating the full and the empty band. It follows that at low temperatures (below the Peierls transition temperature) the organic conductor becomes a semiconductor (or even an insulator if the energy gap between the two bands is wide enough). Among the organic metals we find many compounds which become superdielectrics at low temperatures (12–180 K), with a dielectric constant $\varepsilon \cong 3000$ and a strong anisotropy ($\varepsilon_\parallel/\varepsilon_\perp \cong 500$).

Another surprising property of the one-dimensional organic metals is their transition to the superconducting state, first discovered in 1979 for the compound $(TMTSF)_2^+(PF_6)^-$: at 0.9 K and 12 kbar pressure this organic metal is converted into a superconductor. It was later shown that other salts of composition $(TMTSF)_2^+X^-$, where $X = AsF_6$, TaF_6, SbF_6, and ReO_4, become superconductors at low temperatures and high pressures; the salt $(TMTSF)_2^+(ClO_4)^-$ is a superconductor at 1.2 K even under normal pressure.

The superconductivity mechanism in organic superconductors is still not clear. The formation of Cooper electron pairs and their organised motion in the superconducting state may be controlled by coordinated vibrations of the lattice, and in particular by vibrations of the anion chains (as in classical metallic superconductors). However, a different mechanism (proposed by Little in 1964) is also possible: the motion of the Cooper pairs is controlled by waves of electron polarisation travelling along the side chains. The classical mechanism of superconductivity seems the more likely to apply to the organic metals so far synthesised.

Many inorganic and mixed salts have also been shown to have a near-metallic electrical conductivity. They include the platinum salts $K_2Pt(CN)_4Cl_{0.3}\cdot 3H_2O$ and $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$, the mercury salts $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$ (where $\delta = 0.14$), and also sulphonitride $(SN)_x$, a polymer with metallic conduction. The last three compounds also show superconductivity. The molecular organisation of their crystals is discussed in section II.

Synthetic organic metals, superdielectrics, and superconductors have only recently come to the fore in science: their discovery has created an entirely new field in materials science, with attractive prospects. This field includes some unusual magnetic materials: organic ferromagnetics, whose synthesis is being intensively studied at present.

Chemistry plays an important role in agriculture and medicine. The chemical problems in these areas are fundamental: creating new and effective medicinal preparations (in particular, anticarcinogens), immobilising drugs and immunological

substances on the macromolecules of synthetic or natural polymers in order to increase their effectiveness and to extend their useful life, and developing pesticides, agricultural chemicals, pheromones, and other biologically active compounds. This group of topics includes the development of gel polymers and of synthetic polymeric materials for artificial organs used in surgery, and the modification of their surface to produce antithrombogenic properties. Another important problem is the development of artificial blood substitutes (for example, the perfluorohydrocarbons, which are chemically passive, have no metabolic activity in the organism, and offer a high oxygen capacity, recently shown to be due to complex formation between the oxygen and the fluorine atoms of the fluorinated molecules.

Even this list of materials is not exhaustive, and it is being continually extended. Because of the rapid developments in technology and in the adjacent scientific areas it is difficult to predict which materials will be most widely applied in the near future: it is important for all chemists to remember that the creation of new substances and materials is the fundamental aim of chemistry, and that all their efforts should continue to be devoted to the achievement of this aim.

VI. CHEMICAL TECHNOLOGY

The previous section dealt with existing and likely future developments in chemistry: we shall now consider the methods by which these developments can be realised, i.e. we shall discuss new methods and new principles in chemical technology. Improving existing technologies and developing new technologies is one of the main responsibilities of chemical science. Simplicity, dependence on few stages (preferably, one stage), reliability, moderate energy requirements, high operating speed and yield, continuous operation, absence of residues, acceptance of untreated raw materials, these are the main criteria to be aimed at in new technological developments.

Undoubtedly the central place among the new technologies belongs to catalysis. At present 85% of all industrial processes, responsible for 70% of all chemical production, are based on catalysis. Processes offering a high selectivity and operating speed, economically attractive, and with low energy requirements can be discovered and developed only by using catalysis. This state of affairs has traditionally been found in both heterogeneous and homogeneous catalysis. Significant advances have been made, and many highly effective processes have been adopted by industry, but even greater prospects are seen in advances whose application is still awaited. These include metal-complex catalysis, which allows many reagents to be converted directly into the wanted products without intermediate synthetic stages. For example, the carbonylation of methanol to give acetic acid can take place on rhodium complexes with a methanol selectivity of 99%, and the oxidation of ethylene to acetaldehyde on palladium catalysts has a selectivity of ~95%. Highly effective processes of hydroformylation, the direct synthesis of aromatic isocyanates from nitroaromatic compounds, the synthesis of vinyl acetate from ethylene and acetic acid, and other valuable processes have been developed. The high selectivity of metal complex catalysis is found also in electrochemical processes (for example, the electrochemical oxidation of olefins in the presence of osmium salts gives an almost 100% yield of glycols).

The phenomenon of catalytic metathesis is being studied as a path to the industrial production of new organic compounds and new materials, especially macrocycles, and unusual substances like catenanes (cyclic molecules whose rings are "threaded" through each other like the links of a chain). The synthesis of a catenane from a cyclic diene can be represented schematically as follows:



The first stage is the formation of an inner loop which then becomes fixed by a metathesis reaction; the final result is a catenane.

In another interesting development catalytic processes are conjugated so that the energy evolved by one reaction is used to stimulate another. This possibility exists both in heterogeneous and in homogeneous metal complex catalysis. A good example of conjugated catalytic reactions in cells is the synthesis of ATP by the oxidative phosphorylation of ADP followed by the use of the energy evolved in this reaction to stimulate energy-deficient reactions (including "difficult" reactions such as the biological reduction of molecular nitrogen).

The metal-complex catalysts in the present state of development have a number of shortcomings which can partially (or, on occasions, wholly) offset their advantages. The most serious of these is the need to generate a molecular organisation for the catalyst which ensures long-lived operation of each active centre without decomposition, coupled with ready access of the reacting species to this centre and easy removal of the reaction products. The following principles are being studied as a means of achieving this organisation: the immobilisation of the active centres on the surface of a solid, the "clusterisation" of a group of active centres on solid surfaces (an approach which almost totally eliminates the distinction between homogeneous and heterogeneous catalysis), and the introduction of active centres into the molecular structure of organic crystals (for example, between the planes of carbon atoms in graphite).

A promising approach is the immobilisation of homogeneous complex catalysts in gel polymers, i.e. the chemical or quasi-chemical bonding of the catalyst to a macro-molecule. The immobilisation principle is very close to the operating principle of natural enzymes, which consist of metal-organic catalysts incorporated in the structure of protein macromolecules and whose economy and efficiency are unrivalled. This principle of catalyst organisation offers one fundamental advantage: it can be applied to processes which require the participation of several active catalytic centres (as in the enzyme nitrogenase, in which two active centres contribute to the reduction of nitrogen). The immobilisation of active centres on macromolecules followed by control of the molecular conformation can be used (if necessary) to produce "many-centre" catalysis.

The immobilisation principle is often treated as an enzyme modelling principle: this is a very important and forward looking new attitude in chemical research. A closely related and actively investigated topic is catalysis on immobilised enzymes, which offers attractive prospects in artificial food technology (the synthesis of proteins, aminoacids, and glucose), in medicine, in the chemical analysis of biologically active compounds, in immunology, in micro-energetics (especially in fuel cells, see section VII), and in organic synthesis. Though this work is still on a modest scale because of the high cost of enzymes, current developments in biotechnology and genetic engineering should make enzymes more accessible and increase their "practicality", thus leading to the adoption of immobilised enzymes as an important element of the chemical technology of the future.

Catalysis should play an important role in the new technologies of natural gas and petroleum treatment to give valuable chemical products: the key element in these processes will probably be the catalytic activation of saturated hydrocarbons (especially methane). In view of the world shortage of

energy, great interest is shown in the development of low-energy and high-yield technologies for the treatment of solid fuels (coal, shales, peat, wood cellulose, etc.), aimed at producing hydrogen, carbon monoxide, and artificial petroleum and petrochemicals.

An equally pressing problem is the treatment of inorganic raw materials (ores and minerals). We require improved flotation techniques, more selective flotation reagents, and extractants offering a more quantitative separation of non-ferrous and rare metals and of fluorine and other elements. Chemical methods of metal extraction have long been used in metallurgy (for example, the cyanide method of gold extraction), but their importance is now increasing because of the exhaustion of the richer ores. New technologies can be developed on the basis of organic compounds such as complexones and extractants which react selectively with the ions of the given metals and transfer them from the complex ore into the solution. We could witness the development of a new branch of metallurgy: solvato-metallurgy, differing from traditional metallurgy in not requiring energy-wasteful melting processes.

"Microbiological" metallurgy offers even more attractive prospects. It is based on the ability of some micro-organisms to "treat" ores and selectively extract certain metals from them. These chemolithotrophic (literally, "rock-eating") micro-organisms live in water and they obtain their life-supporting energy from the enzymatic oxidation of inorganic substances, thus "freeing" the metal from its ore and transferring it to the aqueous solution. The large-scale microbiological production of copper is already carried out in several large mining concerns; in the USA more than 10% of the copper production uses this method, and uranium production by the same method is planned. In principle, cultures of micro-organisms which selectively "produce" any wanted metal could be "grown" by genetic engineering: this approach is part of an important new scientific area, biotechnology, which seems likely to expand the possibilities of chemical technology on a vast scale.

Another important success of modern chemistry was the discovery of the reduction (fixation) of molecular nitrogen by homogeneous catalysts. We now await the corresponding development of an industrial nitrogen fixation technology offering a high operating speed and selectivity and a low energy consumption. A similar problem exists in respect of carbon dioxide: an inorganic raw material available in almost limitless quantities. Catalysis can be expected to play a key role in solving this problem. The catalytic utilisation of CO_2 for the synthesis of substances currently listed as "petrochemical" and expected to be in short supply in the very near future should be treated as a pressing chemical problem. Some initial work in that direction has already been reported: we know that the interaction of CO_2 with hydrogen on Ni, Co, and Ru catalysts gives methane, whereas methanol is obtained on oxide catalysts. There are also non-catalytic methods of fixation of CO_2, but they are much less cost-effective. For example, the electrolysis of an aqueous solution of CO_2 and sodium sulphate was shown to produce methanol (in these experiments the current source was a gallium arsenide solar cell).

Combustion processes play an important role in chemistry. They are mainly used in chemical energetics, to produce thermal and mechanical energy. The problem includes the combustion of gases in engines, and the gasification and combustion of liquid and of solid fuels. The main partner of the fuel in combustion processes is oxygen (free, or bound), and the main products are water and carbon dioxide. Combustion technology is continuously advancing, and wider applications are being found. These include mixing-chamber ignition in internal combustion engines, the organisation of combustion within the seam to improve the yield of petroleum deposits, underground gasification in coal mines, etc. All these problems are important, and no effort should be spared in seeking their solution.

Interesting new possibilities were recently identified in the use of combustion processes in industrial inorganic synthesis. A new type of heterogeneous combustion process, not involving oxygen, was discovered: the combustible material is a high-melting metal (Ti, Zr, Hf, Nb, Ta, etc.), and the oxidiser is a non-metal (B, C, Si, molecular nitrogen, hydrogen, etc.). Using combustion processes in these systems a new technology was developed: the self-propagating high-temperature synthesis of high-melting inorganic compounds and materials. The advantages of the technique include low energy consumption, high operating speed, the production of substances and materials having a prescribed composition, physicochemical properties, particle size, and porosity, high-purity products, simple technological design, and ecological purity.

The new technology is being rapidly assimilated in inorganic synthesis: it has already been used to produce more than 200 compounds, including carbides (TiC, ZrC, HfC, NbC, SiC, SC, Cr_3C_2, B_4C, etc.), mixed carbides (TiC–WC, TiC–WC–Mo_2C, TiC–ScC, etc.), nitrides (TiN, ZrN, NbN, TaN (cubic, and hexagonal), BN (cubic), AlN, Si_3N_4), single-phase solid solutions of nitrogen in Ti and Zr, borides (TiB_2, TaB, CrB, NbB, MoB, MoB_2, MnB, NiB, LaB_6, etc.), silicides ($MoSi_2$, $TiSi_2$, Ti_5Si_3, $SrSi_2$, $TaSi_2$, etc.), compounds of S and Se with Nb, Ta, W, Mo, V, Nd, and the mixed chalcogenides $WNbS_2$ and $MoNbS_2$, hydrides (TiH_2, ZrH_2, NbH_2, ScH_2, etc.), intermetallics (NiAl, FeAl, NbGe, NiTi, etc.), solid solutions of carbide nitrides of variable composition (TiN–TiC, TaC–TaN, NbC–NbN, etc.), and solid inorganic alloys and composites (TiC–TiB_2, WC–Co, B_4C–Al_2O_3, Vn–Fe, etc.). All these materials are refractory, super-hard, and wear resistant, and they are used in various areas of technology as hard alloys, abrasives, wear resistant and thermally stable coatings, high-temperature heating elements, alloy steels, fire-resistant materials, etc.

The physicochemical mechanism of this process (the motion of a high-temperature combustion region, leaving a trail of synthesis products, (see Fig.7) offers a number of additional technological possibilities, including the direct preparation of refractory articles of any shape without going through the material production stage; this facility avoids the difficult technological process of forming the refractory material into the desired shape. The new technology is being developed very rapidly because it has firm scientific foundations as well as offering attractive prospects.

Interesting effects have been observed in materials under the combined effects of high pressure and shear deformation: these conditions lead to a number of unusual reactions such as the formation of salts by the interaction of solid metals and solid organic acids, the polymerisation of benzene and other monomers which do not polymerise under normal conditions, the penetration of metal atoms into graphite through the reaction of graphite with solid metals, the formation of solid solutions from a mixture of metal powders, etc. These are apparently the conditions met in shock waves, though in the latter the non-isothermal compression and the shear deformation take place in times of 10^{-12}–10^{-6} s (as opposed to static conditions). Many unusual chemical effects take place in shock waves: the conversion of graphite into diamond, the synthesis of metal nitrides and of boron carbide and nitride, the polymerisation of benzene, etc. The further development and improvement of these technological possibilities is of great interest.

The creation of photochemical technologies such as photolithography is of definite (though specialised) interest. However, there are two problems of more general interest in which

photochemical processes play a major role: silverless photography and the fixation of solar energy (the latter will be examined in more detail in section VII, devoted to chemical energetics).

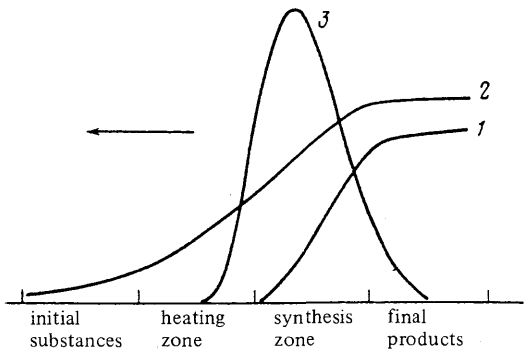


Figure 7. Motion of the combustion zone during self-propagating high-temperature synthesis: *1*) conversion, *2*) temperature, *3*) rate of evolution of heat; the arrow denotes the direction of the combustion wave.

The search for silverless light-sensitive materials and the development of new photographic techniques based on these materials have been stimulated not only by the world shortage of silver (though this is often quoted as the main incentive) but also by the special requirements of modern technology. Significant advances have been made in the synthesis of silverless photosensitive materials of various types (diazotype, vesicular, photochromic materials, etc.), which offer unique properties including high resolution, colour capability, absence of the development stage, reversibility of information recording, and the possibility of repeated use of the same photographic material. The most important problem still outstanding is to improve the light sensitivity of these materials (to the level of 10^7 cm^2 J^{-1} or better). Various suggestions have been made for increasing the quantum yield of the formation of the product responsible for the development of an image. These include the use of radical chain reactions (for example, photo-induced polymerisation), photostimulated phase transitions (for example, the crystallisation of an amorphous substance in the *cis* form stimulated by the presence of the *trans* isomer formed from the *cis* isomer under the influence of light), and catalytic reactions (for example, redox reactions of metal ions "set free" from inactive complexes by exposure to light). The latter include enzyme catalysis reactions: under the influence of light the enzyme is converted from an inactive into an active state, and the image-forming materials are produced as a result of the photo-activation. The term photoenzography has been applied to this new type of photography.

Silverless photography is being developed along several different paths at present, and the best approach has not yet been identified. Sensitisation, which offers higher sensitivity and wider spectral limits (as it does with silver-based photographic materials), is also being studied in conjunction with the new materials.

Plasma-chemical and laser-chemical technologies are also of interest, and have been applied in a number of processes. For example, some evidence of isotope separation by laser chemistry has been observed, but the yield of the method appears to be low. Radiation-chemical technologies are of far greater practical significance because of the large-scale construction of powerful nuclear reactors and of the on-going integration of chemical technology with nuclear energetics. Radiation chemistry has now penetrated the technology of rubber and resin cross-linking and modification, and is widely used in the production of plastics, polymers, and composites as well as in the sterilisation of medical products. Radiation-chemical techniques also offer attractive prospects in chemical energetics (see section VII).

Photochemical, plasma-chemical, and laser-chemical technologies occupy an important place in an important area of modern industry: microelectronics, and their potential applications in this area are still far from being exhausted. The technologies are aimed at the deposition of metallic, oxide, or semiconducting thin films and epitaxial layers by the thermal, photochemical, or plasma-chemical decomposition of metal-organic compounds in the gas phase or by the laser-chemical decomposition of the same compounds adsorbed on the surface. The advantages of this technology include a high purity of the product, relatively low operating temperatures, the possibility of depositing coatings of any type on any surface in any sequence, and generally good adhesion of the layers. Further advantages are the possibility of doping the semiconductors by decomposing metal-organic compounds with laser or electron beams, and the possibility of preparing photographic stencils and protective or diffusion masks without resorting to photolithography or to chemical etching. Similar technologies can be used to prepare super-pure metallic or semiconducting coatings, and magnetic materials (ferrites, magnetic tapes, etc.) with particles of micron or sub-micron size. Almost all the elements of microelectronics (conductors, resistors, semiconductors, dielectrics, microcircuit elements, or even the entire microcircuits) can now be prepared by these techniques.

Many of these processes have already been adopted by industry, but even greater technological possibilities remain to be exploited. The development and improvement of technological methods of using metal-organic compounds in microelectronics is a problem of the first importance. Together with organic semiconductors and metals, and their use in electronics (see section II), the use of metal-organic compounds in microelectronics is a new area of work which could be called organic microelectronics. This is yet another striking example of the integration of different sciences, leading to the birth of new technologies.

This integration has also produced a new and promising technology: the nuclear chemical synthesis of elements, which could be described as a modern "alchemy". We know that semiconductor devices require silicon of the highest purity, doped with phosphorus. The distribution of the doping element (i.e. of the phosphorus in the silicon) must be extremely uniform, and an adequate uniformity is difficult to achieve by chemical methods of doping. A brilliant solution of this problem relies on the fact that as a result of neutron irradiation a silicon atom absorbs a neutron and is rapidly converted into a stable phosphorus isotope by beta-decomposition. This process results in very uniform doping and has already been adopted on a production scale.

This is just one example of the "alchemical" introduction of a required chemical additive. The inverse problem (purification of a material) is also soluble in principle: this approach

replaces the multistage, complex, and expensive chemical purification by neutron irradiation, resulting in transmutation ("alchemical" conversion) of harmful impurities into harmless atomic species.

Nuclear-chemical technology has been used to synthesise a large group of chemical elements (for example, plutonium, technetium, and the entire transuranic group). Furthermore, in the case of some elements which are usually extracted from the atmosphere or from the earth by conventional techniques (for example, xenon, palladium, platinum) the nuclear-chemical technology could have economic advantages. The large-scale practical application of these technologies could have far-reaching economic consequences. Obviously, nuclear-chemical synthesis and its adoption in industry and in materials science will require a well coordinated effort from scientists in nuclear and neutron physics and in nuclear chemistry and radiochemistry. Chemists must be prepared to contribute to the development of this promising branch of modern (and future) chemistry.

VII. CHEMICAL ENERGETICS

The development of effective methods of converting chemical energy into other forms of energy and the creation of chemical means of storing energy in high-energy substances are two areas being actively developed in present-day chemistry, which can be combined under the title of chemical energetics. Its place in modern energetics is still relatively modest, but some predictions of future energy requirements and of the energy structure of world economics (which we shall not attempt to analyse here) foresee an important role for chemical energetics in the future.

The development of methods of converting chemical energy into other forms of energy is one of the oldest problems known to mankind. For many thousands of years it had only one solution: the combustion of high-energy substances (fuels, such as coal, petroleum, gas, wood, peat, and shale). In spite of the very great technological progress in the organisation of combustion processes in order to maximise their efficiency this method remains economically the least attractive. The direct conversion of chemical into electrical energy (i.e. the combustion of the fuel in an electrochemical fuel cell) is a far more effective method of conversion. The development of electrocatalytic methods of combustion and of methods of raising the energy conversion efficiency in fuel cells is one of the fundamental problems in modern chemistry. Important advances have been made towards these goals, and electrochemical energetics are now applied in practice but on an industrial scale still too small to justify classifying the electrochemical approach as "large-scale energetics".

A special variant of the chemical fuel cell is the biochemical cell, whose operation depends on the use of immobilised enzymes to carry out oxidation–reduction reactions. For example, hydrogenase immobilised on a graphite electrode can oxidise molecular hydrogen, producing a hydrogen potential on the electrode. On a second electrode oxygen can be reduced to water by using an oxidase enzyme immobilised on graphite (for example, polyphenol oxidase). The combination of these two half-cells offers an ecologically clean biochemical fuel cell with a high efficiency. Of course, these cells also have some serious shortcomings (short life, the need to purify the fuel to avoid poisoning the enzyme, etc.), but their further development and improvement could be useful.

Among the other methods of converting chemical energy we should mention chemiluminescence, i.e. the generation of light in chemical reactions, and the generation of coherent radiation in chemical lasers.

Another important branch of chemical energetics is the development of cost-effective methods of producing high-energy substances such as hydrogen, methane, etc., which are convenient to use, easily transportable, and capable of storing energy for indefinitely long periods. The most important energy carrier of this type is hydrogen, whose purest (and practically inexhaustible) source is water. The production of hydrogen from water is a problem of strategic importance. Another equally important problem is the development of effective methods of utilising solar energy. These two problems are closely interrelated. We know that solar energy is an important source of energy, and that the only practical method of exploiting it in large-scale energetics is the development of photo-hydrogen energetics.

Various methods of obtaining photo-hydrogen from water have been described; the simplest is the electrolysis of water using electrical energy generated by semiconductor energy converters (Si, GaAs, CdSe, etc.). For a light conversion coefficient of 14% (the normal efficiency of modern silicon photocells) and a 70% utilisation factor of the electrical energy in the electrolytic cell we obtain an overall efficiency of ~10% in the conversion of solar energy into photo-hydrogen. This approach is still expensive and unattractive for large-scale application (the "bottle-neck" being the high cost of the semiconductor photo-converter), but it seems reasonable to devote further effort to it, and to examine (in particular) the possibility of using organic semiconductors.

An alternative approach is photoelectrocatalysis, i.e. the electrolysis of water on a semiconductor surface (for example, TiO_2) coated with a deposited catalyst (for example, metallic platinum). A hole-electron pair is generated in the semiconductor by photolysis, and the electron migrates towards the Pt where it reduces the water to molecular hydrogen, whereas the hole migrates towards the TiO_2 surface and oxidised the water to molecular oxygen. This approach is also relatively ineffective at present, but it has a promising future (through the selection of more suitable semiconductors, the modification of their surface, etc.).

The most attractive path to photo-hydrogen production at present is the third: the identification of molecular photocatalytic and photosensitised systems. It is the nearest approach to natural photosynthesis, which can be interpreted most simply as the photogeneration of an electron and a hole through a series of intermediate steps: the ultimate result is the reduction of CO_2 to carbohydrates (by the electron) and the oxidation of the water to oxygen (by the hole). The only difference between molecular photocatalysis and photosynthesis is that in the former the electron reduces the water rather than CO_2, and therefore the process is also called artificial (or abiogenic) photosynthesis.

These studies have met some serious problems, many of which have already been fully formulated and are being actively solved. The two most important problems in this area are: 1) to ensure the separation of the charges created in the primary photolysis act, so as to prevent their recombination by the inverse reaction, and thus to increase the efficiency of the photolysis; 2) to separate the secondary charge carriers and to prevent their premature recombinations (i.e. their annihilation) so as to ensure their participation in useful oxidation–reduction reactions with the water. Various methods of overcoming these problems have been suggested, all based on the specific attributes of the supermolecular organisation of the photoprocess (see section IV). In model systems both the half-reactions have been realised separately: the reduction of water to hydrogen and its oxidation to oxygen. There are also reports of the combination of these half-reactions into a single process, but we are still a long way from the creation of an effective and economically viable process.

Abiogenic photosynthesis is of interest also because of the possibility of exploiting visible light, whereas photoelectrolysis and photoelectrocatalysis on semiconductors offer a high sensitivity only with ultraviolet radiation, which is present only in small amounts in the solar spectrum.

The radiation-chemical method of producing hydrogen from water offers good prospects, especially in conjunction with high-temperature thermolysis. It relies on the joint application of radiation and heat from nuclear reactors. In the direct, low-temperature radiolysis of water the yield of hydrogen is low because of the reverse recombination of the hydrogen atom with a hydroxyl group. However, at high temperatures the yield of hydrogen increases as a result of the reaction

$$H+H_2O\rightarrow H_2+OH$$

To maximise the hydrogen yield we must remove the hydroxyl from the reaction system. This can be done by using an acceptor with a high effectiveness and selectivity towards hydroxyl: carbon monoxide, which reacts with hydroxyl as follows:

$$OH+CO\rightarrow CO_2+H$$

Thus in the presence of CO the process becomes a chain reaction, which often increases its effectiveness and the hydrogen yield. The overall balance equation for the chemical products is

$$H_2O+CO\rightarrow H_2+CO_2$$

In practice these conditions lead to the chain reduction of water to hydrogen coupled with the oxidation of CO to CO_2; chain initiation is radiation-chemical. The same process can be used for the direct conversion of carbon and water into hydrogen and carbon dioxide:

$$C+2H_2O\rightarrow CO_2+2H_2$$

Other thermodynamic cycles leading to the reduction of water to hydrogen are being studied at present: they all rely on the use of waste heat from nuclear reactors, and all can be classified as variants of hydrogen energetics.

Lastly, chemical energetics and the synthesis of high-energy substances should not be confined to the production of photo-hydrogen. We need to develop the principles by which chemical reactions can be coupled so that the energy evolved by one reaction can be utilised in a high-energy synthesis by another reaction (as in the well known synthesis of ATP and high-energy substances in coupled biochemical reactions). The realisation of these principles and of chemical systems based on them, resembling molecular heat engines, would be an important milestone in both chemical technology and chemical energetics.

Equally attractive is the prospect of the direct conversion of mechanical into chemical energy (for example, the direct mechano-synthesis of calcium carbide from the carbonate, or of hydrogen from water). The mechano-synthesis of high-energy substances is possible, in principle, through chemical reactions under pressure and in the presence of shear deformation (see section VI). Of course, the replacement of hydroelectric stations by hydro-hydrogen stations seems a flight of fantasy at the moment, but the prospect is entirely realistic and worthy of scientific effort.

VIII. ECOLOGICAL CHEMISTRY

The problems of chemical ecology were created by man himself as a result of the continuous (and, during the past century, almost explosive) growth in the industrial activity of mankind. Hence, these problems are artificial to a great extent. However, it would be naive to assume that they can be solved merely by eliminating all sources of ecological pollution, by creating effluent-free (closed) technologies, etc. Some man-made effects in the environment are now too widespread to be reversible, others are slowly reversible, and their elimination would require a great effort and a long time, and a third group of effects are the unavoidable consequences of various technologies (for example, waste products from the nuclear energy industry, contamination from the working of petroleum-bearing underwater shelves, etc.). Hence we need to develop and formulate scientific principles for the elimination, normalisation, and control of harmful or dangerous anthropological effects in the environment, and ecological chemistry should play a major role in this work.

Man-made effects are most marked in the atmosphere, stratosphere, and hydrosphere. Sources of chemical pollution of the atmosphere include the emission of the oxides of nitrogen, sulphur, and carbon, of aromatic hydrocarbons, olefins, and saturated hydrocarbons. The main problem in atmospheric chemicstry is the analysis of chemical reactions in this multi-component system, the quantitative formulation of their kinetics, and the analysis of oxidation processes by molecular oxygen assisted by photolysis due to sunlight. From such a "catalogue" of atmospheric chemical reactions and their kinetics and energetics we must formulate generalised kinetic models of the chemistry of the atmosphere, including processes such as heat and mass transfer (by diffusion and convection of air masses), the development of temperature gradients, humidity, intensity of the solar radiation, etc. The aim of these models is to identify the most harmful components of atmospheric pollution and to predict their long-term and global consequences. The real (and even pressing) need to solve this problem was underlined by recently discovered effects such as "acid rain", which has caused serious economic and ecological losses in the eastern United States, in Scandinavia, in Europe, and in other regions.

Similar problems are found in the chemistry of the stratosphere. However, they include an additional problem of global importance: the fate of the ozone layer, whose role in determining the life support capability of our planet is well recognised. Concern for the fate of the ozone layer in the stratosphere was first expressed in 1970 in connection with the flight of supersonic aircraft emitting oxides of nitrogen. The latter initiate the decomposition of ozone by the reactions

$$NO+O_3\rightarrow NO_2+O_2$$
$$NO_2+O\rightarrow NO+O_2$$

whose sum produces the overall reaction

$$O_3+O\rightarrow 2O_2$$

with long kinetic chains. Chain generation is by the reaction

$$N_2O+O\rightarrow 2NO$$

and the photolysis of oxygen and ozone provides the source of oxygen atoms.

In addition to supersonic aircraft, the natural life processes of nitrogen fixing bacteria (which are a part of the overall nitrogen fixation cycle) contribute to the emission of N_2O. Furthermore, N_2O is a product of the metabolism of nitrogen-containing fertilisers.

It is now clear, however, that the combined threat from all these sources to the ozone layer has been overstated, and that the main threat is from the Freons (especially $CFCl_3$ and CF_2Cl_2), now used on a large scale as refrigerants, aerosol

propellants, etc. The photolysis of these compounds produces chlorine atoms which decompose the ozone:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

The chlorine atoms catalyse the overall chain process, in which the chain length can reach 10^5. Chain breaking is produced by the reaction of the chlorine atom with methane, but the concentration of methane in the stratosphere is very low (of the order of 1.5 parts per million).

It has been calculated that if the use of Freons continues at the present level the amount of ozone in the stratosphere could be decreased by 17% by the end of the century (a dangerously high figure). Therefore one of the main problems in ecological chemistry is to produce reliable models of stratospheric chemistry, based on the quantitative kinetics and on the quantum yields of all the elementary thermal and photochemical reactions, allowing for data on the spectroscopy and optics of the atmosphere and of the stratosphere and for recent information on the complex formation of molecular oxygen with fluorine atoms in fluorinated molecules. The latter effect is important because the formation of complexes between Freons and oxygen and their photochemical decomposition could be an effective method of breaking down the Freons in the atmosphere.

The protection of the hydrosphere is an important part of ecological chemistry. The problem includes effluent waters from industrial and agricultural activities and natural effluents containing toxic chemicals, fertilisers, and pesticides leached from the soil. The analysis and control of chemical contaminants and the development of reliable and simple methods of purification have long been recognised as the traditional problems of the ecological chemistry of the hydrosphere.

The contamination of the oceans by petroleum products is another important problem. Petroleum and petroleum chemicals distributed as a thin film on the water surface are oxidised by molecular oxygen (partly by enzyme reactions and partly photochemically) by the well known radical chain mechanism. The resulting products (especially the organic acids) are surface-active substances which cover vast water surfaces and affect the evaporation of the oceans, with serious effects on the biology of the ocean through the dissolution of the oxidation products (many of which are poisonous) and through the alteration of the oxygen balance of the ocean.

The ecological effects of the contamination of the ocean and their long-term consequences have not yet been evaluated: studies of the chemistry of the process, and of their kinetics and thermodynamics, are required in order to establish predictive models.

Chemical and ecological effects in the atmosphere, stratosphere, and hydrosphere can lead to perturbations of the thermal balance and to serious meteorological and climatological consequences. Therefore an overall "chemical" monitoring of the environment is required. It should be organised as a control of the chemical state of the atmosphere, stratosphere, and hydrosphere, aimed at detecting sources of pollution and analysing the evolution of these contaminants under natural conditions. The problem includes the development of methods of chemical analysis with high-level quantitative characteristics (which are also needed in technology and in materials science, see section IX).

Lately, an important topic in ecological chemistry is the evaluation of the chemical effects of socially hazardous undertakings such as the production and testing of substances for chemical warfare and nuclear tests. Their danger and social unacceptability should be obvious not only from social considerations but also from the standpoint of ecological chemistry.

IX. DIAGNOSTIC AND ANALYTICAL CHEMISTRY

Progress in chemical materials science and in chemical industry would be impossible without a corresponding progress in diagnostic and analytical chemistry. The improvement of existing principles and methods of chemical analysis, and the development of new ones, are important problems in modern chemistry.

It is often said that chemists have received many valuable gifts from physicists: optical and vibrational spectroscopy, X-ray diffraction, neutron and electron diffraction, electronic and nuclear magnetic resonance, etc. This point of view is understandable, but not entirely correct, since the opposite view could be put forward. Undoubtedly, in addition to normal analytical methods (traditional chemical analysis, neutron activation and electrochemical analysis, chromatography, emission spectroscopy, etc.) physical methods are widely used in chemistry for the analysis and characterisation of substances, materials, and processes (X-ray and photoelectron spectroscopy, mass spectrometry, low-energy electron diffraction, Mössbauer spectroscopy, dynamic light and neutron scattering, microwave spectroscopy, etc.). Chemists have made a major contribution to the development of these methods and to the expansion of their metrological and analytical capabilities. Effective advances in analytical and diagnostic chemistry can be expected from the application of general advances in chemistry, physics, and instrument design.

Modern technology requires improved analytical and metrological systems for controlling technological processes, the state of the reactor and of its surroundings, and for detecting the need for corrective action at a usefully early stage thus ensuring stable and reliable process control. This type of system should convert the information on the state of the materials, of the processes, and of the surroundings into signals which can be processed in the normal way, and it should be small, sensitive, and fast acting, so as to respond to rapidly changing conditions.

The sensor detectors are systems of this type: they are cheap and small, fast-responding devices designed to measure the parameters of the surrounding medium and of the technological process (pressure, temperature, chemical composition, etc.), and they have been intensively developed in recent years. They include electrochemical sensors (using solid or traditional electrolytes), piezo-sensors (used for the microweighing of adsorbed gases), sensors based on ion-selective membranes, and others. However, the most sensitive devices are those which use semiconductors as the sensing element. They differ from sensors of other types in being smaller, more reliable, and in responding more rapidly to changes in concentration.

The use of metal-oxide and other semiconductors for determining concentrations in gases relies on the change in impurity conduction of these materials upon the adsorption of certain gases. Adsorption sensors are usually prepared from the semiconducting oxides of various metals (Sn, Zn, Ti, Ni, V, and some others). The initial conductivity of these semiconductors is low, and therefore even the adsorption of a small amount of gas causes a large change in resistance of the detector. The threshold sensitivity of these primary converters is 10^6–10^8 cm^{-3}.

The sensors can measure the concentration of different gases: H_2, O_2, H_2O, NO, CO, CO_2, H_2S, SO_2, hydrocarbons, etc. However, their selectivity is low, due to the specific properties of adsorption and diffusion through selective membranes. The extent to which selectivity is a requirement in semiconductor sensors depends on the application envisaged. In many cases a modest selectivity is acceptable (when it is known that only a particular combination of gases can be met

under the experimental conditions). For example, sensors for methane used in coal-mine gas detectors do not need a high selectivity, and their ability to respond to many reducing gases in addition to methane is unimportant.

However, in other situations we need to determine gas concentrations in an atmosphere of unknown composition. In this case the sensor should respond to changes in the concentration of only one component of the atmosphere. A proposed solution of this problem relies on the use of a set of different low-selectivity sensors.

Sensors containing different semiconductors and operating at different temperatures give different responses to the adsorption of different gases. The temperature dependence of the conductivity of a pellet of SnO_2 baked at 500 °C and treated in SO_2 at 350–500 °C for 15 min during the adsorption of different gases is shown in Fig. 8. We conclude from these plots that by an appropriate choice of sensor and of working temperature we can produce a set of detectors which can jointly identify uniquely any composition of the gas mixture to which they are exposed. The signals from the sensors can be converted into a system of equations which are solved by a micro-processor so as to determine the concentration of all the components in any gas mixture. This method of solving the problem of producing a selective detector is more promising and rational than attempting to construct an intrinsically selective sensor, which usually results in a serious loss of sensitivity.

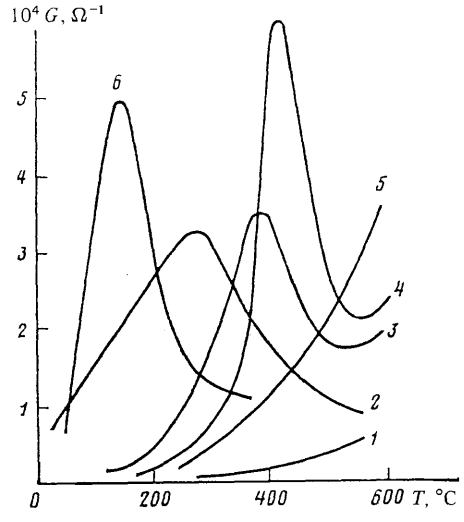


Figure 8. Temperature dependence of the sensitivity of a sensor based on SnO_2 baked at 500 °C and activated with SO_2 (1000 ppm) at 350–500 °C: *1*) air, *2*) SO_2, *3*) n-pentane (1000 ppm), *4*) ethylene and butane (0.7%), *5*) methane and ethane (1000 ppm), *6*) hydrogen sulphide (40 ppm).

These sensors have a relatively high sensitivity. A typical threshold sensitivity is 1 ppm (part per million) or less, but for some gases it can be a few ppb (parts per billion). In the detection of active gas particles (atoms, radicals, excited molecules) the sensitivity of semiconductor sensors is even higher (up to 10^{-6} mg cm^{-3}). It can even exceed the physiological sensitivity of the human nose.

One of the most important characteristics of the sensor is its response time, i.e. its speed of action. Clearly, the shorter the response time, the sooner can an operator monitoring the displayed signal take the required corrective action in response to changes in composition within the reactor or in the surroundings. The response times of the sensors can be long, reaching several minutes in the piezo-detector and in detectors relying on solid electrolytes, but in semiconductor sensors the response time can be ~10 ms.

The main advantage of semiconductors over other types of sensor is their small size and weight. The size of any semiconductor device is determined primarily by the size of the dielectric substrate on which the semiconductor is carried: this is not usually more than a few square millimetres, with a thickness of the order of 1 mm. A whole set of semiconductor detectors can be deposited on a single dielectric substrate to give a multiple assembly weighing only a few grammes.

An important problem in the development of sensor devices is their technological feasibility on a large scale. In recent years micro-electronic and computer technology have reached such a high level that information processing and display systems working in real time can be produced routinely in industry. Semiconductors can therefore be produced in large batches by existing microelectronic technologies.

The development and formulation of new analytical and metrological principles, systems, and devices is another problem in modern chemistry. The range of applications is almost limitless: from the analysis of the chemical composition of substances from the composition of their vapour, even at very low pressures, to the detection of trace impurities and of toxic substances in the atmosphere and to the control of the state of materials, articles, and assemblies. For example, the ageing of concrete produces various gases, varying in amount and composition as the ageing proceeds. A diagnosis of the age of concrete and a prediction of the likely collapse of concrete structures can be based on this effect. This new principle in technological non-destructive testing can be applied to the diagnosis of the state and likely future behaviour of the most diverse materials and structures. Obvious application are in geophysics, vulcanology, gas and petroleum prospecting, and other branches of science and technology.

The principles of analysis with semiconductor detectors can also be applied successfully in medical diagnostics. For example, the composition of gaseous metabolic products in a living organism (evolved in breathing) and the presence of some trace components can be used to diagnose functional anomalies in certain organs and to detect illnesses at an earlier stage than by using conventional methods of diagnosis.

X. CONCLUSIONS

Chemistry, like any other science, solves or tries to solve a very large number of problems covering a wide range of level and scale, economic importance, and general value, and it is important not to lose sight of the main outlines of chemical science and of their changes with time in the ever-increasing flow of publications.

The aim of the present review was to define the most important and most up-to-date directions in modern chemistry. We tried to assess these directions objectively, and to avoid any bias from our personal scientific interests and commitments. We could be accused of presenting an incomplete or cursory

analysis of the problems, but as any thoughtful reader will understand a fully comprehensive discussion is out of the question in a review of this type.

Every scientific endeavour, every scientific search (including chemical ones) should answer three main questions: what, why, and how. The first question concerns what to seek, what to do, what is the value of the search; the second asks why should the work be done, are the expected results useful, or necessary, where can it be applied, how can it affect various areas of science, technology, and production; the third question asks what is the most rational method of carrying out the work, and how to choose the best, quickest, and most reliable and economical path towards an unambiguous solution of the problem as defined. This logical organisation of scientific research corresponds to that used in the present review: part of the review deals with the questions "what" and "why" (sections V–X), and part with the question "how" (sections II–IV).

We hope to take up the theme of this paper again in a few years, and to assess the extent to which the problems outlined here have been solved and the correctness of the present predictions.